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Homogenization of $Pb(Zr,Ti)O_3$ by use of molten phase

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Abstract

A method for a homogenization of $Pb(Zr,Ti)O_3$(PZT) was developed. Powders of PbO and TiO_2 were added into a powder of PZT prepared by the ordinary method. This mixture was heated above the melting point of PbO for several periods of time. PbO and TiO_2 formed a molten phase. After the heat treatment, it was quenched. PbO phase in the sample was removed by dissolving with acetic acid. The chemical homogeneity of the PZT phase was figured out using $\beta\cos\theta$ vs. $\sin\theta$ plots. This analysis showed that the chemical homogeneity in the PZT phase was improved very quickly.

Keywords: Flux methods; Homogenisation; $Pb(Zr,Ti)O_3$; Powder preparation

1. Introduction

$Pb(Zr_xTi_{1-x})O_3$ (PZT) is a solid solution[1] between $PbTiO_3$ and $PbZrO_3$ and has excellent piezoelectric properties.[2] Generally it is prepared through a reaction among oxides of constituent cations.[3] We have reported[4–6] that PZT prepared by such a method has inhomogeneity of composition (compositional fluctuation). The compositional fluctuation affects many electrical properties.[7–9] It also causes incorrect interpretations of measured values.[6,10]

Many efforts have been made to obtain homogeneous solid solutions.[11–14] All those efforts were focussed on the homogeneity of the raw materials. In this study a new method to enhance the homogenization process through the diffusion during the firing was developed. In order to enhance the diffusion, a molten phase whose principal component is PbO was used.

2. Experimental procedure

Powders of PbO, ZrO_2 and TiO_2 were mixed thoroughly with agate mortar and pestle. The mixture was pressed into disks (about 12 mm in diameter and 2 mm in thickness) and fired at 1100°C for 2 h in a closed magnesia double crucible[15] with an equimolar mixture of PbO and ZrO_2 which provides PbO vapor atmosphere.[16] PZT was formed by this firing. This is the ordinary method to prepare PZT. The composition of the PZT was $Pb(Zr_{0.3}Ti_{0.7})O_3$. $Pb(Zr_{0.3}Ti_{0.7})O_3$ such prepared is abbreviated as PZT-30. PZT-30 was ground and mixed with PbO and TiO_2. The ratio of PbO:TiO_2 was set to the composition of the molten phase which can coexist with PZT-30 at 1100°C at the equilibrium.[17] The mole ratio of PbO to PZT-30 was 2:1. The composition of the molten phase was calculated from the phase equilibrium. The mole ratio of PbO:TiO_2:ZrO_2 was 0.649:0.349:0.002. ZrO_2 was not added into the mixture because the amount can be neglected. This mixture was fired in a sealed platinum crucible at 1100° for 15, 30, 60 and 120 min. At the firing temperature, PbO and TiO_2 formed a molten phase. After the firing, it was quenched. PbO phase in the sample was removed by dissolving with acetic acid. Samples so treated are tentatively named PZT-30[tr15 min], PZT-30[tr30 min], PZT-30[tr60 min] and PZT-30[tr120 min] depending on the treating period of time in the molten phase.

For the measurements of powder XRD (MXP18VA/HF, MAC Science Inc.), a Cu target was used with a monochromator. As an optical system for the qualitative measurements, a divergence slit of 1°, a scattering slit of 1°, and a receiving slit of 0.15 mm were used. The net peak width (β) caused from the sample was figured out using MXP System Standard Software (MAC Science Inc.). Widths at half-maximum intensity for Si were used as a standard.

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3. Results and discussion

Fig. 1 is a phase diagram of $PbTiO_3$–$PbZrO_3$–PbO system[17] at 1100°C. In this system PZT having composition S_0 can coexist with a molten phase of the point L. Generally, PZT has a compositional fluctuation, i.e. a mixture of compositions around the average composition. Now we consider a situation that a powder of PZT, which consists of compositions ranging from S_1 to S_2, is heated with a molten phase L. Particles in the PZT sample having composition S_1 cannot coexist with the molten phase L in equilibrium. TiO_2 component in such particles will be dissolved into the molten phase and its composition will be shifted towards S_0. On the other hand, for particles having composition S_2, TiO_2 component in the molten phase will be precipitated into PZT phase, the composition of the particles being shifted towards S_0. Every particle has such a tendency.

The situation of PZT particles dispersed in the molten phase (L) is shown in Fig. 2 schematically. For particles whose concentration of TiO_2 is higher than that in equilibrium, TiO_2 component dissolves into the molten phase. For particles whose concentration of TiO_2 is lower than that in equilibrium, TiO_2 component moves from molten phase into the particles. The overall migration of TiO_2 component is from particles having high TiO_2 concentration into those having low TiO_2 concentration. This will cause a homogenization of the PZT sample. The most part of the migration path is in the molten phase (liquid phase). In general, the migration rate in liquid phases is much higher than that in solid phases.

In the solid state reaction, the entire part of the migration path is in the solid phase. It has been shown that the homogenization rate for the solid state reaction is slow.[18,19] This is caused from the low diffusion rate in the solid phase. This difficulty may be improved by the

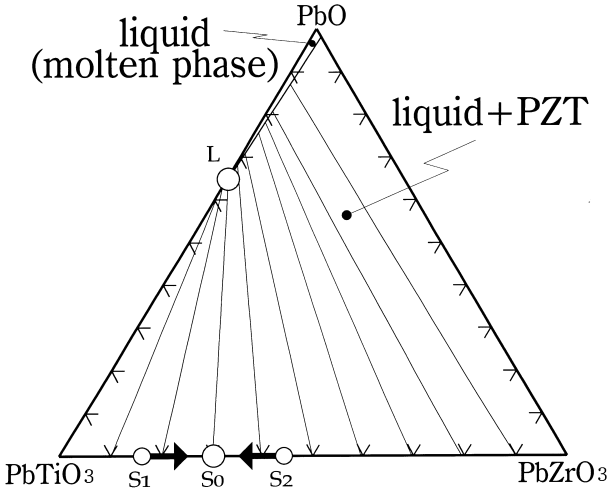

Fig. 1. Phase diagram of PbO–$PbTiO_3$–$PbZrO_3$ system at 1100°C.

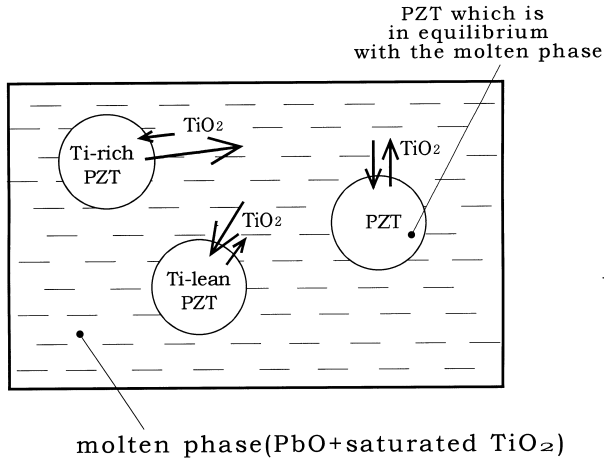

Fig. 2. Process for the elimination of the compositional fluctuation.

treatment of the PZT powder in the molten phase, because the most part of the migration path during the treatment is in the molten phase.

XRD pattern of the sample treated with the molten phase at 1100°C for 2 h (PZT-30[tr120 min]) is shown in Fig. 3. It consists of two different perovskite phases. One is the original PZT phase. The composition of the other phase was estimated from its lattice constants. It was almost $PbTiO_3$. This was formed from the molten phase. While molten PbO (at 1100°C) can dissolve TiO_2, solid PbO (at room temperature) cannot dissolve TiO_2. When the molten phase is cooled, TiO_2 component in the molten phase segregates, reacts with PbO and forms $PbTiO_3$. From the phase diagram, the composition of the perovskite phase formed from the liquid phase is calculated to be $Pb(Zr_{0.008}Ti_{0.992})O_3$, which can be regarded as $PbTiO_3$. In this study, we pay attention to the original PZT phase. The separation of the second phase is a future subject. It is worthwhile to obtain PZT phase that has almost no compositional fluctuation, even if it exists with other phases, because such PZT phase provides much information of homogeneous phase.[10]

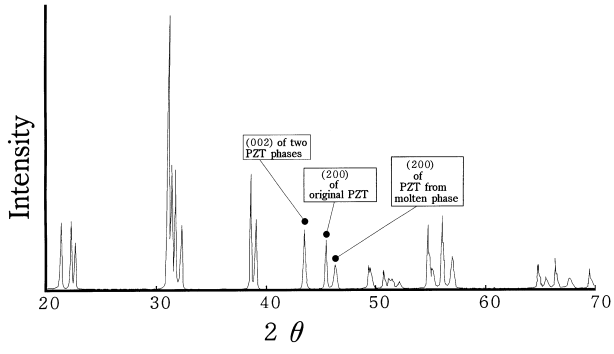

Fig. 3. X-ray diffraction pattern for PZT after the treatment (PZT-30[tr120 min]).

The compositional fluctuation in PZT can be evaluated using plots of $\beta\cos\theta$ vs. $\sin\theta$. It has been demonstrated that the slope of those plots can be used as a parameter of the degree of the compositional fluctuation.[4] The slope of the plots for a sample having no compositional fluctuation is zero, and the slope increases as the compositional fluctuation increases. Plots of $\beta\cos\theta$ vs. $\sin\theta$ for PZT-30 is shown in Fig. 4 (●). The slope of these plots implies that this sample has a large compositional fluctuation.

Plots of $\beta\cos\theta$ vs. $\sin\theta$ for PZT-30[tr15 min], PZT-30[tr30 min] and PZT-30[tr60 min] are shown in Fig. 4 (□, ◇, △). The slope of the plots decreased as the treating period increased. The samples treated with the molten phase have small or no gradient, which means this treatment is effective for the elimination of the compositional fluctuation.

For the comparison, PZT-30 was heated for 60 min without the molten phase. The plots of $\beta\cos\theta$ vs. $\sin\theta$ for this sample were also plotted and shown in Fig. 4 (■). This rate of the homogenization is slow and typical as shown before.[4]

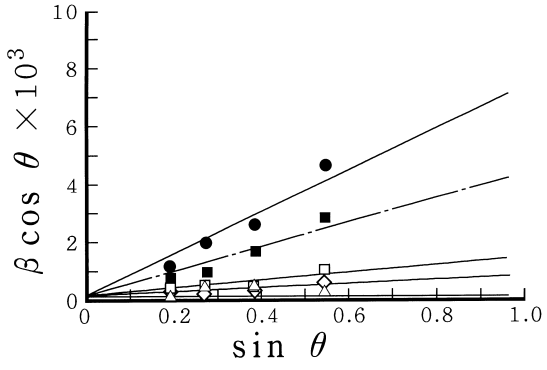

Fig. 4. Plots of $\beta\cos\theta$ vs. $\sin\theta$ for PZT ●: PZT-30; □: PZT-30[tr15 min]; ◇: PZT-30[tr30 min]; △: PZT-30[tr60 min]; ■: after the heat treatment at 1100°C for 1 h without the molten phase.

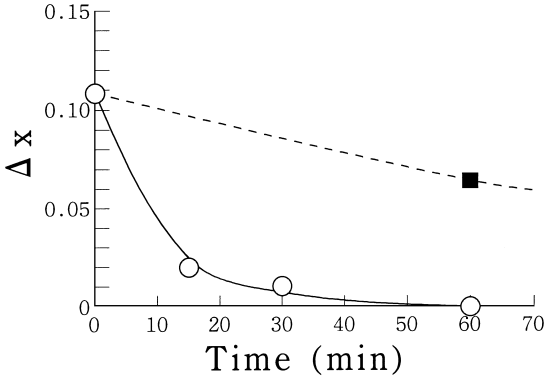

Fig. 5. Compositional fluctuation width of PZT as a function of heating time. ○: PZT after the heat treatment at 1100°C with the molten phase ■: PZT after the heat treatment at 1100°C without the molten phase.

The fluctuation width of composition can be calculated from the slope of these plots.[4] Fig. 5 shows the compositional fluctuation width as a function of heat treating period. For the samples heated with molten phase, the compositional fluctuation width was decreased quickly. The compositional fluctuation width for the sample heated without liquid phase was also plotted in this figure (■). According to the previous study, the compositional fluctuation remained even for a sample heated for 16 h. Considering these results, it is obvious that the treatment in the molten phase is very effective for the homogenization of the PZT solid solutions.

4. Conclusions

A method for the homogenization of PZT was developed. PZT was heated at 1100°C with molten phase of $PbO + TiO_2$. The homogenization rate by this treatment was much faster than the normal heat treatment.

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